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Photoluminescence of the African scorpion "Pandinus imperator"

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Abstract

The luminescence of the scorpion's outer shell has been shown to be due to fluorescence of very short lifetime (nanoseconds). The emission and excitation spectra have been determined, and the potential biological significance of this photoluminescence is discussed.

Keywords: African scorpion "Pandinus imperator"; Photoluminescence

1. Introduction

The observation of luminescence is widespread in the natural world and can, in most cases, be described as bioluminescence or photoluminescence [1]. The former results from highly exergonic chemical reactions, such as the decomposition of peroxides, and the latter requires external excitation light to form the electronically excited states of suitable organic molecules.

The luminescence of scorpions, which has been known for many years, is an example of photoluminescence. In total darkness, these animals show no detectable emission of light; in the presence of a UV light source (usually a medium-pressure mercury arc), a faint blue–green emission can be observed from the whole body, and this property has been used by scorpion hunters to detect these animals by night.

Although there have been some reports concerning this photoluminescence in the scientific literature, these have been either qualitative or clearly mistaken [2]. In a collaboration between the Museum of Natural History and the Institute of Physical Chemistry of the University of Fribourg, we have made detailed measurements of the luminescence emission and excitation spectra of the species "Pandinus imperator". We have also measured the luminescence lifetimes. It was beyond the scope of this research project to separate and analyse the luminescent molecule(s), but a reasonable hypothesis can be derived from the spectra. We conclude this study with a discussion of the possible biological significance of this photoluminescence.

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2. Experimental details

The luminescence emission and excitation spectra were recorded on a home-built spectrofluorometer described previously [3]. The light source was a 150 W xenon arc, since the line spectra of mercury arcs are not suitable for the measurement of the excitation spectra. All the spectra were corrected for the instrumental response. For the emission spectra, the reference was 1,1′,4,4′-tetraphenylbutadiene, the corrected spectrum being taken from Berlman [4]. For the excitation spectrum, we chose the dye "acridine yellow", the absorption spectrum of which was recorded on a Perkin–Elmer Lambda 5 spectrophotometer.

The scorpion sample was a piece of a claw, held at an angle such that direct reflection of excitation light could not enter the entrance slit of the emission monochromator.

The dead scorpion, supplied by the Museum of Natural History, had been kept at 77 K in dry conditions. Some attempts were also made to use the outer shell in the form of a powder, but this presents problems of scattered light which makes measurements difficult. It should be noted that the fluorescent dye can be extracted in certain polar solvents, but it is impossible to determine whether or not the chemical structure is modified. For these reasons, we preferred to use the outer shell of the claw as it is in nature.

3. Results and discussion

The luminescence of the scorpion can be readily observed with a medium-pressure mercury arc fitted with a filter which removes the visible part of the spectrum. The main excitation

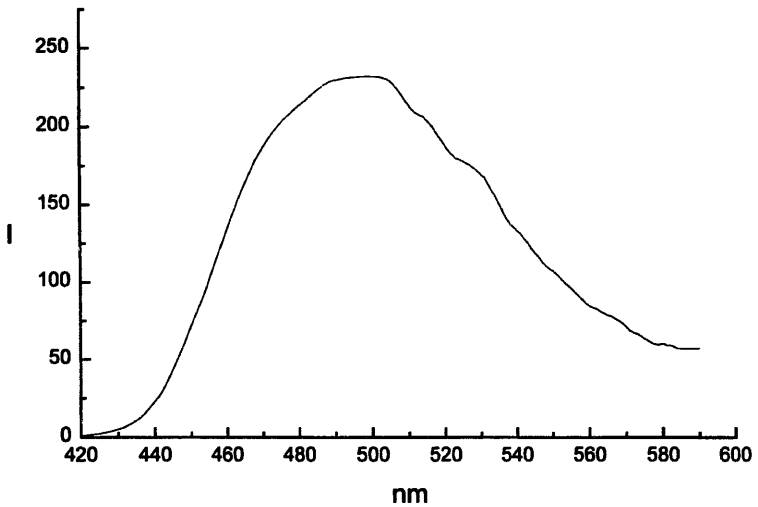

Fig. 1. Luminescence spectrum of the outer shell of "Pandinus imperator". Horizontal axis, wavelength in nanometres; vertical axis, emission intensity in arbitrary units.

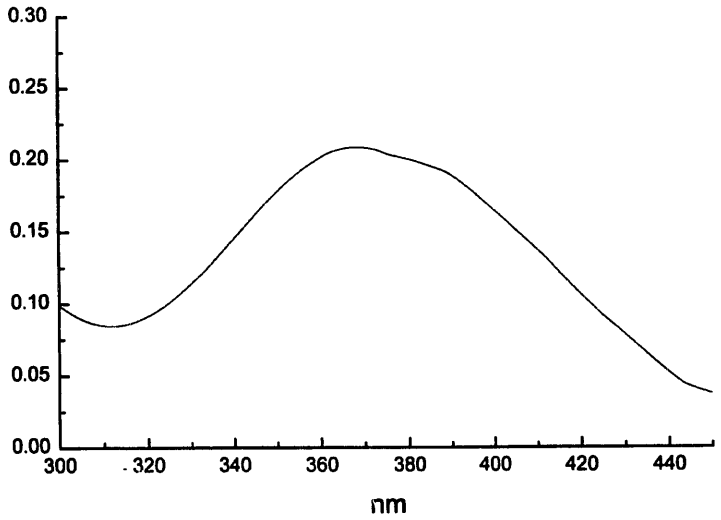

Fig. 2. Luminescence excitation spectrum (same axes as Fig. 1).

light is the line at 365 nm, and the emission spectrum is shown in Fig. 1.

It is clear that this emission cannot originate from a porphyrin-type molecule, which emits at a much longer wavelength. The excitation spectrum is shown in Fig. 2, and this is not dependent on the emission wavelength in the range 440–560 nm. Therefore it appears that the emission originates from a single molecular species, rather than from a mixture of different species.

Since we measured the corrected excitation spectrum, it should correspond to the absorption spectrum of the chromophore. This appears to be the case, since there is a reasonable mirror-image relationship between the emission and excitation spectra.

The emission lifetime was measured with a laser flash photolysis apparatus described elsewhere [5]. The laser pulse has a duration of about 30 ps, and it is immediately clear that the emission must be fluorescence rather than phosphorescence. The lifetime is about 2.5 ns, as shown in Fig. 3.

Since the depth of penetration of the excitation light cannot be determined accurately with such solid samples, only a rough estimate of the luminescence quantum yield can be given; this is quite low, of the order of a few per cent, in keeping with the short emission lifetime.

We have made no attempt to determine the exact nature of the fluorescing chromophore. From a comparison of the known emission and absorption spectra of commonly found biological dyes, the most likely candidates are flavins and flavones [6]. These are widespread in the natural world and their luminescence characteristics are well known.

The observation of the fluorescence of these and other scorpions raises the question of its potential biological significance. Thus bioluminescence, which is a form of chemiluminescence of living organisms, can be involved in the processes of mating (e.g. fireflies) and feeding (e.g. deep sea fish). In this case, the luminescence is concentrated in certain specific organs. However, for the scorpions considered here, the whole body shows a weak photoluminescence. This is

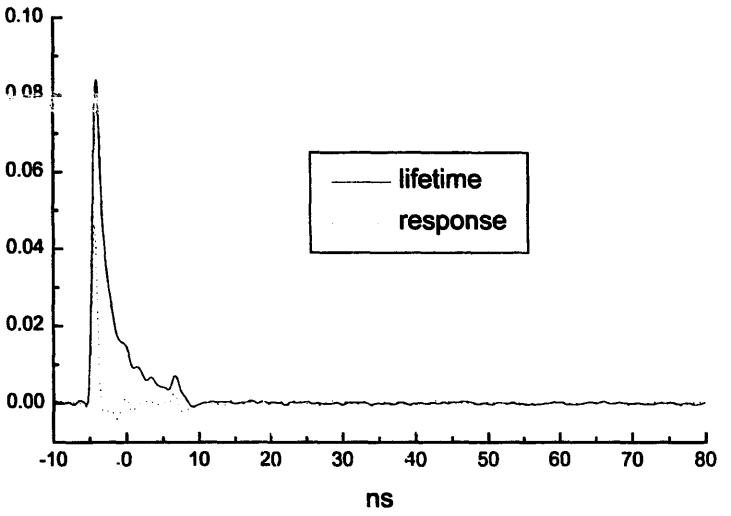

Fig. 3. Decay kinetics of the luminescence: ———, lifetime; · · ·, response. Horizontal axis, time in nanoseconds; vertical axis, intensity in arbitrary units.

quite different as it requires an external light source for excitation. Human scorpion hunters use portable UV lamps to find their prey, but the other predators in the natural world do not have access to such facilities. In addition, scorpions are essentially nocturnal animals, and in the absence of sunlight there is no UV radiation in the desert at night. During the day, scorpions usually remain underground away from the source of UV excitation light. When they are exposed to sunlight, the scattered visible light is far stronger than the weak luminescence, which cannot be detected against such a bright background. The "Pandinus imperator" has in fact a matt black colour in white light.

We conclude that the photoluminescence of these scorpions plays no biological role. It should not be forgotten that luminescence emission is a widespread property of organic substances; therefore it is not surprising that it can be observed from the surface of many plants and animals.

References

[1] P. Suppan, Chemistry and Light, Royal Society of Chemistry, Cambridge, 1994.
[2] G.A. Polis (Ed.), The Biology of Scorpions, Stanford University Press, Stanford, CA, 1990. C. Constantinou, J.L. Clousley-Thompson, Newsl. Br. Arachnol. Soc. 44 (1985) 7.
[3] N. Ghoneim, Y. Rohner, P. Suppan, Faraday Discuss. Chem. Soc. 86 (1988) 295.
[4] I.B. Berlman, Handbook of Fluorescence of Aromatic Molecules, Academic Press, New York, 1971.
[5] P.A. Muller and E. Vauthey, private communication.
[6] B. Brodhun, D.-P. Hälder, J. Photochem. Photobiol. B: Biol. 28 (1995) 39.